

Orbital Order Instability and Orbital Excitations in Degenerate Itinerant Electron Systems

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We present the theory of orbital ordering in orbital-degenerate itinerant electron systems. After proposing the criterion of instability for orbital ordering or orbital density wave ordering, we find that the orbital and the spin-orbital collective excitation spectra in ferro-orbital ordered phase exhibit finite gaps. The anomalous electronic energy spectra manifested in the angle-resolved photoemission spectroscopy (ARPES) and the orbital occupation in the resonant X-ray scattering (RXS) intensities are also presented for the orbital-ordered phase.

One of the most attracting developments in condensed matter physics this decade is to realize the roles of the orbital degree of freedom in the ground states, transport and optical properties in narrow-band transition-metal oxides and other compounds with unfulfilled *d* or *f* orbitals. In these compounds, strong Coulomb interactions and highly anisotropic orbital correlations compel these nearly localized electrons to regularly occupy different orbitals, forming the orbital ordering (OO) [1]. Upon doping from low to high concentration, the carriers, electrons or holes, are introduced into the compounds. One may expect that these carriers bring about frustrated orbital and spin arrangements, and eventually destroy the OO at a small doping concentration. However, it is found that in many such orbital compounds, the OO phase persists over wide doping range, as shown in the phase diagrams of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [2, 3], $(\text{Sr}, \text{Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ [4], and $\text{La}_{1-x}(\text{Sr}, \text{Ca})_x\text{MnO}_3$ [1], etc. This arises the question that why the correlated electrons are still OO in the presence of many carriers? Especially for the relatively wide band ruthenates, the radius of *4d* electrons is large and the *4d* electrons may exhibit itinerant character, in comparison with the localized *3d* electrons in manganites and vanadates. How do these *4d* electrons become localized over wide doped region? Understanding the formation of OO and the low temperature properties in the orbital-degenerate itinerant electron systems becomes the focus of this Letter, which will also help us understand the orbital properties in localized electron systems.

As we know that the OO in orbital-degenerate narrow-band correlated electronic systems arises from the inter-orbital Coulomb repulsion U' [1]. In an orbital-degenerate itinerant electron system, the inter-orbital Coulomb repulsion is usually not completely screened, then it may separate the two degenerate orbitals at a magnitude order of U' , and modify the orbital occupation at each site. Most probably, it is expected that the inter-orbital Coulomb interaction may play the similar role to the intra-orbital Coulomb repulsion, U , in itinerant elec-

tron systems [6], and modulate the orbital distribution to form orbital density wave or OO phase. The conventional multi-orbital itinerant electron magnetism theory [8] ignored the possibilities of the formation of OO or orbital density wave phase. The recent experiment by Kubota et al. [2] showed that in relatively wide band *4d* compound $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{MnO}_4$ the metallic phase and OO coexist over the temperatures below 300 K, this fact is curious from the OO scenario in localized electron systems. These experimental and theoretical facts appeal for new theory for the orbital physics in itinerant electron systems.

In this Letter we investigate the orbital physics in orbital-degenerate itinerant electron systems. We propose a criterion for the orbital instability for OO or orbital density wave ordering in the two-orbital itinerant electron model, and show that, similar to the Stoner condition in itinerant electron magnetism, the inter-orbital Coulomb interaction should be larger than a critical value for the occurrence of OO or orbital density wave state, independent of the fine structures of the degenerate bands; the energy spectra of the orbital wave and the spin-orbital wave exhibit finite gaps, which are distinguished different from the spin wave spectrum. Furthermore, we discuss the manifestations of the the electronic spectra in the angle-resolved photoemission spectroscopy (ARPES) and the orbital occupation resonant X-ray scattering intensity (RXS) in the ferro-orbital ordered itinerant electron systems.

The Hamiltonian of two-orbital degenerate itinerant electron systems reads,

$$\begin{aligned} \hat{H} = & \sum_{\mathbf{k}, \sigma} \sum_{\alpha\beta} \epsilon_{\mathbf{k}\alpha\beta} \hat{c}_{\mathbf{k}\alpha\sigma}^\dagger \hat{c}_{\mathbf{k}\beta\sigma} + U \sum_{i\alpha} \hat{c}_{i\alpha\uparrow}^\dagger \hat{c}_{i\alpha\uparrow} \hat{c}_{i\alpha\downarrow}^\dagger \hat{c}_{i\alpha\downarrow} \\ & + U' \sum_{i\sigma\sigma'} \hat{c}_{i1\sigma}^\dagger \hat{c}_{i1\sigma} \hat{c}_{i2\sigma'}^\dagger \hat{c}_{i2\sigma'} - J \sum_{i\sigma\sigma'} \hat{c}_{i1\sigma}^\dagger \hat{c}_{i1\sigma'} \hat{c}_{i2\sigma}^\dagger \hat{c}_{i2\sigma'} \\ & + J \sum_{i\alpha \neq \alpha'} \hat{c}_{i\alpha\uparrow}^\dagger \hat{c}_{i\alpha'\uparrow} \hat{c}_{i\alpha\downarrow}^\dagger \hat{c}_{i\alpha'\downarrow} \end{aligned} \quad (1)$$

The off-diagonal components of the non-interacting energy spectrum of electrons $\epsilon_{\mathbf{k}\alpha\beta}$ ($\alpha \neq \beta$) are usually finite, here for clarity, we consider only the diagonal hopping. We assume that the electron occupations of the

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two bands are the same to make sure that the system is para-orbital in the absence of interactions. In the present itinerant electron systems, considering the screening effect, we adopt the relation of the intra- and the inter-orbital Coulomb interactions U and U' , and the Hund's coupling J_H : $U > U' > J_H > 0$, rather than the relation: $U=U'+2J$ [5].

As the response to the external field, when spin or orbital ordering occurs, the response function of the spins or that of the orbitals diverges near the disorder-order transition point. The spin and the orbital dynamical transverse susceptibilities [6] read,

$$\chi_s^{-+}(\mathbf{q}, \omega + is) = i \int_0^\infty dt e^{i\omega t} \langle [S_q^-(t), S_{-q}^+(0)] \rangle$$

$$\chi_o^{-+}(\mathbf{q}, \omega + is) = i \int_0^\infty dt e^{i\omega t} \langle [\tau_q^-(t), \tau_{-q}^+(0)] \rangle \quad (2)$$

where the spin lift operator is $S_q^+ = \sum_{\mathbf{k}m} \hat{c}_{\mathbf{k}+\mathbf{q}m\uparrow}^\dagger \hat{c}_{\mathbf{k}m\downarrow}$ and the orbital pseudospin lift operator is denoted as $\tau_q^+ = \sum_{\mathbf{k}\sigma} \hat{c}_{\mathbf{k}+\mathbf{q}1\sigma}^\dagger \hat{c}_{\mathbf{k}2\sigma}$. The spin and the orbital dynamical transverse susceptibilities in the paramagnetic and para-orbital metal regime are obtained in the random phase approximation. Although the full expressions of these susceptibilities are complicated, it is not different to find that in the present itinerant electron system, the spin instability for the spin density wave of wavevector \mathbf{q} occurs at:

$$-\frac{\eta'_1(\mathbf{q}) + \eta'_2(\mathbf{q})}{\eta_1(\mathbf{q})\eta'_2(\mathbf{q}) + \eta_2(\mathbf{q})\eta'_1(\mathbf{q})} \leq U + J \quad (3)$$

with $\eta'_m(\mathbf{q}) = 1 + (U - J)\eta_m(\mathbf{q})$ for the orbital index m , and

$$\eta_m(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q},m\downarrow} - f_{\mathbf{k},m\uparrow}}{(\epsilon_{\mathbf{k}+\mathbf{q},m} - \epsilon_{\mathbf{k},m}) + \Lambda_m}$$

here $\Lambda_m = U(n_{m\uparrow} - n_{m\downarrow}) + J_H(n_{\overline{m}\uparrow} - n_{\overline{m}\downarrow})$. In the paramagnetic phase, $n_{1\uparrow} + n_{2\uparrow} = n_{1\downarrow} + n_{2\downarrow} = n_0/2$. At $\Lambda_m = 0$, $-\eta_\alpha(0)$ gives rise to the DOS per site for α -band [7]. n_0 denotes the average occupation number of the electrons at each site. Restricting Eq.(3) to the single orbital case, $\eta_2(0)$ vanishes and $-\eta_1(0)$ gives rise to the DOS per site at Fermi energy E_F , the conventional Stoner condition for the single-band itinerant electron ferromagnetic order [8]: $U\rho(E_F) \geq 1$, is thus unambiguously arrived.

The orbital instability for the orbital density wave ordering of wavevector \mathbf{q} occurs at:

$$\frac{\lambda'_\uparrow(\mathbf{q})\lambda'_\downarrow(\mathbf{q})}{\lambda_\uparrow(\mathbf{q})\lambda'_\downarrow(\mathbf{q}) + \lambda_\downarrow(\mathbf{q})\lambda'_\uparrow(\mathbf{q})} \geq J \quad (4)$$

with $\lambda'_\sigma(\mathbf{q}) = 1 + U'\lambda_\sigma(\mathbf{q})$, and

$$\lambda_\sigma(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q},2\sigma} - f_{\mathbf{k},1\sigma}}{(\epsilon_{\mathbf{k}+\mathbf{q},2} - \epsilon_{\mathbf{k},1}) + \Lambda_\sigma}$$

here $\Lambda_\sigma = (U - U')(n_{2\sigma} - n_{1\sigma}) + (U' - J)(n_{1\sigma} - n_{2\sigma})$, and in the para-orbital phase, $n_{1\uparrow} + n_{1\downarrow} = n_{2\uparrow} + n_{2\downarrow} = n_0/2$. In the paramagnetic and para-orbital phase, $n_{1\uparrow} = n_{2\uparrow} = n_{1\downarrow} = n_{2\downarrow}$. $-\eta_\alpha(0)$ gives rise to the DOS per site for α band [7]. When the system is OO and paramagnetic, the condition, $n_{1\uparrow} = n_{2\uparrow} = n_{1\downarrow} = n_{2\downarrow}$, does not hold. This situation is ignored in the theory of the multi-orbital itinerant electron magnetism [8]. In the spin order and OO phase, the magnetization, $m = n_\downarrow - n_\uparrow$, and the orbitalization, $\tau = n_2 - n_1$, are the order parameters describing the polarization degrees of spins and orbitals.

We now focus on the ordered orbital ground state. The ordered phase can be ferro-orbital or orbital density wave of \mathbf{q} when the ferro-orbital or the orbital density wave instability occurs:

A). Occurrence of Ferro-orbital Ordering

In the paramagnetic and para-orbital itinerant electron systems with two degenerate bands, $f_{\mathbf{k},1\uparrow} = f_{\mathbf{k},1\downarrow} = f_{\mathbf{k},2\uparrow} = f_{\mathbf{k},2\downarrow}$, the divergence of the orbital dynamical transverse susceptibility at $\mathbf{q} = 0$ gives rise to the criterion of ferro-orbital ordering

$$(U' - 2J_H)\varrho_{12} \geq 1 \quad (5)$$

at $T = 0$ K, where $\varrho_{12} = -\lambda_1(\mathbf{0}) = -\lambda_2(\mathbf{0})$ is the coalition DOS per site of each spin channel near the Fermi surface in the itinerant electron systems. Obviously the inter-orbital Coulomb repulsion U' plays the same role in OO as the intra-orbital repulsion U in magnetism; while considering the Pauli exclusive principle and the Hund's coupling, the spins of the electrons tend to align in the same direction in different orbitals, so the Hund's coupling is unfavorable of the orbital polarization, making against to the emergence of the OO phase, as we see in Eq.(5). If the spins are complete polarized, the system is therefore half metallic, the condition for the ferro-orbital ordering instability becomes:

$$(U' - J_H)\varrho_{12} \geq 1 \quad (5')$$

which implies that in the ferromagnetic phase, OO is more easier to occur than the paramagnetic phase. Since in the presence of the Hund's coupling and Coulomb interaction, due to the spin-orbital coupling in Eq.(1), the ordered spin structure favors the OO configuration.

B). Formation of Orbital Density Wave State

Due to itinerant character of the electrons, the orbital of the electrons may be not completely polarized as ferro-orbital ordering, rather, the orbital polarization may vary in different sites, it forms a spatial modulating structure with the characteristic wavevector \mathbf{Q} , i.e., orbital density wave phase. The criterion for the occurrence of orbital density wave phase is:

$$(U' - 2J_H)\varrho_{12}(\mathbf{Q}) \geq 1 \quad (6)$$

in the paramagnetic regime, here $\varrho_{12}(\mathbf{Q}) = -\lambda_1(\mathbf{Q}) = -\lambda_2(\mathbf{Q})$. In the ferromagnetic or spin density wave phase, Eq.(6) will be slightly modified. The conditions

(5) and (6) show that at $T = 0$ K, the orbital-degenerate itinerant electron system is ferro-orbital or orbital density wave order when the inter-orbital Coulomb interaction strength U' is larger than a critical value to separate the two orbitals far enough.

C). Excitations in Ferro-Orbital Ordered Phase

Furthermore, the dynamic instabilities of these response functions in Eq.(2) provide the information of collective and Stoner-type excitations of the spins and the orbitals. In the long wave-length and low frequency limit, we find that the energy spectra of the spin wave and the spin Stoner excitations in the present systems are consistent with the literatures [8], and in analogous with the non-degenerate itinerant electron model with isotropic energy band [6]. Meanwhile, the external perturbation field also stimulates the orbital collective excitations, *i.e.*, the orbital wave in the long wave-length regime. And in the short wave-length regime, the orbital Stoner-type particle-hole excitations are also found. In the long wave-length and low frequency limit, the orbital wave spectrum $\omega_o(\mathbf{q})$ is

$$\Omega_o(\mathbf{q}) = \Delta_o + \xi_o \mathbf{q}^2 \quad (7)$$

in the system with the spherical iso-energetic surface. Here the parameters Δ_o and ξ_o , depending on the band structure and the orbital polarization of the system, represent the gap and the stiffness of the orbital waves. Such kind orbital wave has been observed in narrow-band doped manganites by the Raman scattering experiments [9]. And one also finds that the energy spectrum of orbital Stoner-type excitation, ω_σ , is

$$\omega_\sigma(\mathbf{q}) = \epsilon_{\mathbf{k}+\mathbf{q}1\sigma} - \epsilon_{\mathbf{k}2\sigma} \quad (8)$$

Since the spin angular momentum of the electrons is conserved during the hopping, one observes two independent branches in the orbital single-particle excitations (8).

The difference of the dispersions of between the gapped orbital waves and the gapless spin waves could be understood in the framework of spontaneous symmetry breaking of the continuously symmetric systems. As we know that a remarkable feature of spontaneous symmetry breaking of the continuously symmetric order parameter is the appearance of massless particles: Goldstone bosons [10, 11], posses gapless excitations. Since the multi-orbital itinerant electronic Hamiltonian (1) is invariant under the continuous rotation of the spin operators in the spin space, so the spin wave is the Goldstone bosons without a gap in the energy spectrum. However, the continuous rotation invariance of the Hamiltonian (1) is broken in the orbital space, thus the orbital wave is not a type of Goldstone bosons, therefore the energy spectrum of the orbital waves exhibits a finite gap.

Associated with the gapped orbital wave excitations, we find there exists a novel type of composite excitations, which arises from the interplay between spins and orbital

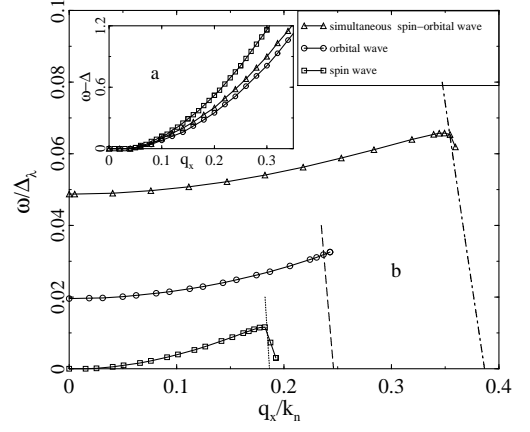


FIG. 1: Dispersion relations of the spin, the orbital and the spin-orbital collective and Stoner-type excitations along the (100) direction in ferro-orbital ordered phase. Dotted lines, long dashed lines and dot-dashed lines denote spin, orbital and simultaneous spin-orbital Stoner excitations, respectively.

degrees of freedom. According to the definition of spin-orbital composite operators [12].

$$\hat{K}_{\mathbf{q}}^+ = \hat{c}_{\mathbf{k}+\mathbf{q}1\uparrow}^\dagger \hat{c}_{\mathbf{k}2\downarrow} + \hat{c}_{\mathbf{k}+\mathbf{q}2\downarrow}^\dagger \hat{c}_{\mathbf{k}1\downarrow}$$

$$\hat{K}_{\mathbf{q}}^- = \hat{c}_{\mathbf{k}+\mathbf{q}1\downarrow}^\dagger \hat{c}_{\mathbf{k}2\uparrow} + \hat{c}_{\mathbf{k}+\mathbf{q}2\uparrow}^\dagger \hat{c}_{\mathbf{k}1\uparrow} \quad (9)$$

the simultaneous spin-orbital dynamical transverse susceptibility becomes:

$$\chi^{-+}(\mathbf{q}, \omega + is) = i \int_0^\infty dt e^{i\omega t} \langle [\hat{K}_{\mathbf{q}}^-(t), \hat{K}_{-\mathbf{q}}^+(0)] \rangle \quad (10)$$

The energy spectrum of the simultaneous spin-orbital excitations can be extracted from the poles of the dynamical transverse susceptibility. In the long wave-length and low frequency regime, the energy spectrum of the collective excitations, or the simultaneous spin-orbital wave, is

$$\Omega_{so}(\mathbf{q}) = \Delta_{so} + \xi_{so} \mathbf{q}^2 \quad (11)$$

An energy gap Δ_{so} is also observed in the energy spectrum, and ξ_{so} denotes the stiffness of the simultaneous spin-orbital wave. The corresponding Stoner-type particle-hole excitation spectrum is

$$\omega_m(\mathbf{q}) = \epsilon_{\mathbf{k}+\mathbf{q}m\uparrow} - \epsilon_{\mathbf{k}\bar{m}\downarrow} \quad (12)$$

We expect that the simultaneous spin-orbital wave (11) and the orbital-dependent particle-hole excitations (8) and (12) could be identified in further resonant Raman experiments.

To understand the low-energy excitations of the ferro-orbital ordered itinerant electron systems, we numerically study the dependence of the energy spectra of the spin wave, the orbital wave and the simultaneous spin-orbital wave on the wavevector, and the corresponding Stoner-type particle-hole pair excitations, the

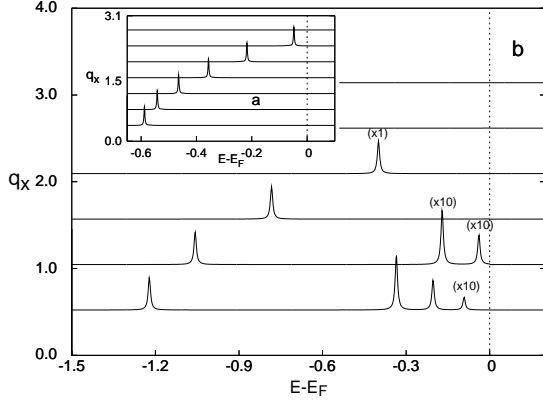


FIG. 2: Variation of electronic spectral function $A(\mathbf{k}, \omega)$ in paramagnetic and para-orbital phase (dot lines), and in ferromagnetic and ferro-orbital ordered phase (solid lines). The theoretical parameters are the same as Fig.1. Wavevector \mathbf{q} is along the x direction (100).

more detailed dispersion relations of these excitations are shown in Fig 1. In the numerical calculation, we adopt the twofold degenerate parabolic energy bands, $\epsilon_{\mathbf{k}1} = \epsilon_{\mathbf{k}2} = (k_x^2 + k_y^2 + k_z^2)/10$ eV, and the electron occupation is quarter-filling. The intra-orbital and inter-orbital Coulomb interactions, $U = 1.55$ eV and $U' = 1.44$ eV, respectively; and the Hund's coupling $J = 0.055$ eV. The corresponding Stoner parameters, k_f is 1.97, 1.61 and 1.97, and Δ_λ is 0.13, 0.11 and 0.24 eV, respectively. We find the z-components of the magnetization and the orbitalization per site, m_z and τ_z , are 0.4 and 0.3, respectively. In the long wavelength and low frequency limit, the gaps of the orbital-wave and the simultaneous spin-orbital wave are 2.25 and 11.38 meV, respectively, which can be seen clearly in Fig.1. In the long wavelength limit, the dispersions of spin wave, orbital wave and the simultaneous spin-orbital wave with respect to the gaps are proportional to q^2 , and the stiffness of the three kind collective excitations, as shown in the inset of Fig.1, are 13.65, 9.81 and 11.38 meV for the spin wave, the orbital wave and the simultaneous spin-orbital wave, respectively.

It is worthy of noticing that in the present orbital-degenerate itinerant electron system, the system remains metallic in the ordered orbital ground state. We find when the spin and orbital disorder-order transition occurs, the degenerate electronic energy spectrum splits into four different subbands in the random phase approximation. The variation of the electronic energy spectra near E_F can be reflected in the angle-resolved photoemission spectroscopy (ARPES). The spectral weight of itinerant electron in the OO and spin order phase is shown in Fig.2. When the system is para-magnetic and para-orbital, there is only one large peak in the intensity of

the ARPES, which is contributed from the degenerate bands, and each band contributes the same weight to the peak, as shown in the inset in Fig.2. As far as the system enters into the ferro-orbital and ferromagnetic phase,

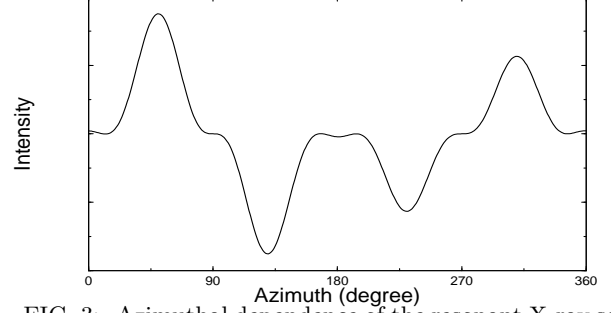


FIG. 3: Azimuthal dependence of the resonant X-ray scattering intensity in ferro-orbital itinerant electron systems. Theoretical parameters are the same as Fig.1.

the peak splits into four peaks, which correspond to the fact that the degenerate bands in orbital disorder phase splits into four different subbands since the degeneracy is lifted as the OO forms, hence the subbands with different weights contribute the four peaks with different height. So the measurement to the spectral functions by ARPES provides an indirect way to observe the orbital phase transitions, and the information of the variation of orbital polarization in multi-orbital itinerant electron systems.

The regularly polarized orbital occupation in narrow-band transition-metal oxides with OO can be manifested in the resonant X-ray scattering (RXS) experiment [13]. In the present ferro-orbital itinerant electron system, according to the scattering theory of ferro-orbital ordering [2], we find the K-edge RXS intensity of 1s-4d event in the ferro-orbital itinerant electron system is significantly different from zero, and the azimuthal angle dependence of the RXS intensity is shown in Fig.3. The period of the RXS intensity is 2π , and the azimuthal dependence of the intensity is very similar to that in ferro-orbital ordered $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$. However we notice that ruthenates are almost three-orbital degenerate, the two-orbital degenerate itinerant electron compound is not found yet. We expect more extensive search for such systems in experiments to examine the present itinerant orbital order theory.

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